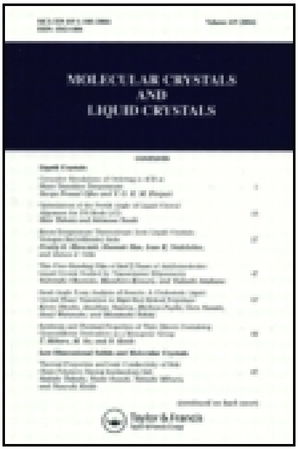

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Intercalation Route to Novel Superconducting Nano-Hybrids

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Version of record first published: 27 Oct 2006

To cite this article: Jin-Ho Choy, Woo Lee, Eue-Soon Jang, Soon-Jae Kwon, Seong-Ju Hwang & Young-Il Kim (2000): Intercalation Route to Novel Superconducting Nano-Hybrids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 479-484

To link to this article: http://dx.doi.org/10.1080/10587250008026185

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 479-484
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Printed in Malaysia

Intercalation Route to Novel Superconducting Nano-Hybrids

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We have adopted novel synthetic strategies, i.e HSAB (hard-soft-acid-base) interaction and interlayer complexation concepts, to develop the superconducting nano-hybrids via intercalation technique. On the basis of these concepts, new series of inorganic-inorganic nano-hybrids, M-X-$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (M = Hg, Ag, Au; X = Br, I; n = 1, 2, and 3) and of organic-inorganic ones, R_2HgI_4-$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (R = organic cation) could be successfully prepared. The magnetic susceptibility measurements for these intercalates reveal that the intercalation of organic chain molecules has little influence on the superconducting transition temperature (T_c) of the pristine compounds, in spite of remarkable basal increments up to ~ 30 Å It has been also demonstrated that the present organic intercalates can be used as effective precursor materials for fabricating the superconducting thin film and nano-particle.

Keywords: intercalation; Bi-based superconductors; nano-hybrid; superconducting nono-particle

INTRODUCTION

We have systematically applied intercalation reaction to layered Bi-based cuprate superconductors to develop new high-T_c superconducting nano-hybrids as well as to investigate superconductivity. Previously an attempt has been made to understand the bonding character of iodine molecules intercalated in $Bi_2Sr_2Ca_nCu_{2n-1}O_y$ (hereafter, referred as Bi2201 for n = 1, Bi2212 for n = 2, and Bi2223 for n = 3, respectively), and we found that triiodide molecular ions are predominantly stabilized in between the Bi_2O_2 double layers due to a partial electron transfer from host lattice to intercalant layer[1]. In the light of such a finding, a new series of inorganic-inorganic and organic-inorganic superconducting nano-hybrids could be successfully developed by applying new synthetic strategies such as hard-soft acid-base interaction and the interlayer complexation concepts. In this report, we summarized our recent studies on the intercalation of HgX_2-, AgI-, AuI-, and organic-salt-intercalated into the $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (n = 1, 2, and 3) superconductors and on the novel preparative routes to Bi-cuprate colloids and their thin films.

EXPERIMENTAL

All the pristine $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (n = 1, 2, and 3) compounds were prepared by the conventional solid state reaction as reported previously[2]. The HgX_2-intercalates (X = Br and I) of Bi2201 and Bi2212 were synthesized by vapor transport reaction between host and guest in a vacuum sealed Pyrex tube at 230 - 240 °C for 4 h[3], whereas the corresponding AgI-intercalates were prepared by heating the mixture pellet of host and Ag metal under iodine atmosphere ($P(I_2)$ = 1 atm) at 170 °C for 3 h and then at 190 °C for 10 h in air[4]. The organic-inorganic hybrids, $[(Py\text{-}C_xH_{2x+1}I)_2HgI_4]\text{-}Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (x = 1, 2, 4, 6, 8, 10, and 12; n = 1, 2, and 3), were also achieved by solvent-mediated reaction between HgI_2-intercalates and alkylpyridinium iodide ($Py\text{-}C_xH_{2x+1}I$) at 40 - 70 °C for 6 h[5]. The physico-chemical properties of these intercalates were characterized by performing powder X-ray diffraction (XRD), X-ray absorption spectroscopic (XAS) analyses, micro-Raman spectroscopic analysis, and dc-magnetic susceptibility measurements, along with chemical analysis by electron probe micro-analysis (EPMA) and thermogravimetric analysis (TGA). In the case of AgI-intercalates, the ionic conductivity was also measured with impedance spectroscopy.

RESULT AND DISCUSSION

Metal-halide intercalation

According to our previous Raman and XAS studies on the iodine intercalates[6], the iodine molecules can be intercalated into lamella host lattice due to the charge transfer between host and guest, where the guest molecules play a role as electron acceptor and the host as electron donor. Based on this result, we were successful in developing a new type of high-T_c superconducting compound, M-X-$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (M = Hg, Ag, Au; X = Br, I; n = 1 - 3) by intercalating various kinds of soft Lewis acids.

From the XRD analyses, the lattice expansion along *c*-axis (Δd) upon intercalation is estimated to be • 6.3 Å for the $HgBr_2$-intercalates and • 7.2 Å for the HgI_2-ones, which indicates that the halogen bilayers are stabilized in the interlayer space of Bi-based cuprate[7]. On the other hand, it is found that the AuI-intercalation leads to the lattice expansion of • 3.25 Å, implying the mono-layered geometry of guest Au-I species. The polarized micro-Raman and EXAFS analyses at the Hg L_{III}- and Au L_{III}-edges could reveal that the intercalated HgX_2 is stabilized as 2-coordinated molecule, whereas AuI as 3-coordinated one, respectively. According to the dc-magnetic susceptibility measurements, all the metal halide-intercalates show bulk superconductivity with a slight T_c depression, compared to the corresponding pristine compounds. The maintenance of superconductivity upon intercalation of metal halide allows us to conclude that the interlayer coupling effect[8] is not a main factor for the T_c depression. In this respect, the T_c evolution upon intercalation should be understood in terms of the charge transfer between guest and host block.

It is worthy to note here that, besides electronic conductivity, the AgI-intercalate shows a high ionic conductivity ($\sigma_i = 10^{-1.4} \sim 10^{-2.6}\ \Omega^{-1}cm^{-1}$ at 270 °C) with an uniform activation energy ($E_a = 0.22 \pm 0.02$ eV). Such a mixed conductivity originates from the unique crystal structure of the AgI-intercalate consisting of ionic conducting AgI layer and electronic conducting host sheet[4,9].

Organic-salt intercalation

Taking into account the fact that the mercury in HgX_2-intercalates is coordinatively unsaturated, it can be expected that the intercalated mercuric halide species could be further ligated by organic/inorganic ligands in the interlayer space of Bi-based cuprates. The XRD and high-resolution transmission electron microscope (HRTEM) analyses for the organic salt-intercalate, $[(Py\text{-}C_xH_{2x+1}I)_2HgI_4]\text{-}Bi_2Sr_2Ca_{n-1}Cu_nO_y$, reveal that the basal increment along *c*-axis changes gradually from 11Å (x = 1) to 32Å (x = 12) depending on the length of alkyl chain. As shown in Figure 1, the long chain organic molecules are regularly interstratified in between oxide blocks[5].

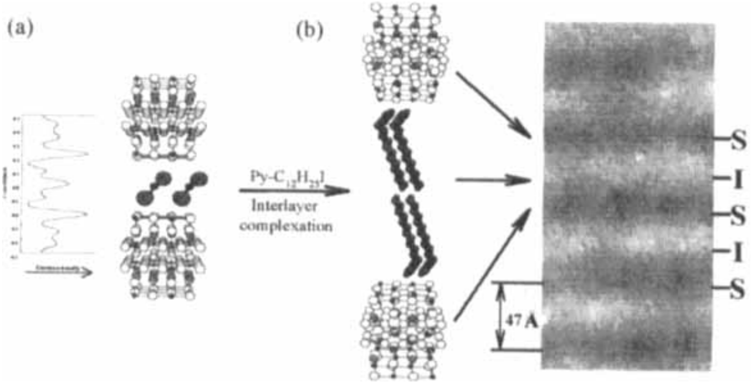

FIGURE 1 (a) Structural model of HgI_2-Bi2212, together with one-dimensional electron density mapping along the c-axis (left). (b) Proposed interlayer structures of dodecylpyridium iodide intercalate of Bi2212, where the anions (HgI_4^{2-}) are omitted here for simplicity. The cross-sectional view of HRTEM of the organic intercalate manifests the organic-salts are regularly interstratified in between the superconducting cuprate blocks with a fashion of superconducting-insulating-superconducting (S-I-S) composite.

The EXAFS analyses on the Hg L_{III}-edge of the organic-salt intercalates manifest that the mercury in these compounds is tetrahedrally coordinated, in contrast to the two coordinated Hg in the HgI_2-intercalate. Such results clarify that the intercalation of organic molecule occurs surely through the interlayer complexation between intracrystalline HgI_2 and *n*-alkylpyridinium iodide, resulting in the formation of bis(*n*-alkylpyridinium) tetraiodomercurate ($(Py\text{-}C_xH_{2x+1})_2HgI_4$.

TABLE 1 Interlayer distance and T_c for $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (n = 1, 2, and 3) and their intercalates

Compounds		c [Å]	Δc [Å]	T_c [K]	ΔT_c [K]
n = 1	Pristine	24.2	–	29	–
	HgI_2	38.4	14.2	25	- 4
	$HgBr_2$	36.8	12.6	27	- 2
	AgI	38.8	14.6	25	- 4
	Organic salts	46.0 ~ 88.0	21.8 ~ 63.8	28 ~ 31	-1 ~ +2
n = 2	Pristine	30.7	–	80	–
	HgI_2	45.0	14.3	72	- 8
	$HgBr_2$	43.3	12.6	75	- 5
	AgI	45.5	14.8	67	- 13
	AuI	37.1	6.5	78	- 2
	Organic salts	52.3 ~ 93.9	21.6 ~ 63.2	80 ~ 81	0 ~ +1
n = 3	Pristine	36.9	–	104	–
	HgI_2	50.5	13.6	96	- 8
	AgI	51.6	14.7	93	- 11
	Organic salts	75.9 ~ 98.1	19.5 ~ 61.2	–	–

According to the dc-magnetic susceptibility measurements, no significant T_c change could be observed upon intercalation of organic salts, suggesting that the charge carrier density of CuO_2 plane plays a main role in determining the T_c, rather than the interlayer coupling effect[8]. For Bi-based layered cuprates, $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ and their intercalates, the interlayer distance and T_c are summarized in Table 1.

Superconducting nano-particles and films

The intercalation of *n*-alkyl chain derivatives can provide a new way of engineering high-T_c cuprates in a molecular level, since it is possible to obtain ultra-thin superconducting particles by exfoliating them into individual sheets. In fact, we were successful in preparing the superconducting colloidal suspension by exfoliating organic-salt intercalates, those which are expected to be excellent precursor materials for the superconducting nano-particles or thin films and wire. AFM height profiles for the delaminated Bi2212 and Bi2223 reveal that the minimum thickness of exfoliated particles is close to the half of the c-axis length of the pristine materials (i.e., 15.3 Å for Bi2212 and 18.6 Å for Bi2223). The superconducting thin film has been also prepared by electrodepositing the superconducting colloids on Ag- or Pt-substrate, and by subsequent heating the deposited film. The film thickness can be easily controlled by adjusting applied voltage and/or deposition time.

Acknowledgment
This work was supported in part by the Korean Ministry of Education (BSRI-98-3413) through the research institute of basic science, Seoul National University and by the Korean Science and Engineering Foundation through the Center for Molecular Catalysis.

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